

Photooxygenation in Polystyrene Beads with Covalently and Non-Covalently Bound Tetraarylporphyrin Sensitizers

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Abstract: Two reaction protocols are described which involve the use of polymer supports as reaction media for photooxygenation processes: 1) The use of polystyrene beads (PS) loaded with tetraphenyl- (TPP) or tetratolylporphyrin (TTP), swollen with the substrate in an appropriate organic solvent and subsequent irradiation under air. Products were isolated simply by dissolution in alcoholic solvents and filtration. 2) Covalently linked tetrasterylporphyrin in polystyrene-divinylbenzene beads were synthesized by emulsifier-free emulsion polymerization and directly used for the photooxygenation protocol described above. The latter alternative allows also the use of less polar solvents for the extraction of the oxygenation prod-

ucts from the polymer beads. From the sensitizer loading degree, an optimal substrate/sensitizer molar ratio of 1,000–2,000 was determined and recyclization is possible for at least five times resulting in a minimum turnover number (with respect to the sensitizer TTP) of 5×10^4 (after five cycles). Both approaches were applied to the ene reaction of singlet oxygen with citronellol (**1**), the regioisomeric pinenes **3** and **5**, and the allylic alcohols **9a–c**, respectively, as well as to the [4 + 2]-cycloadditions of singlet oxygen to sorbinol (**7**) and the chiral diene **11**.

Keywords: allylic alcohols; cycloaddition; ene reaction; photooxygenation; singlet oxygen

Introduction

Type II photooxygenation reactions involve the first electronically excited singlet state of oxygen ($^1\Delta_g\text{-}^1\text{O}_2$), which is formed by energy transfer either from a singlet or a triplet excited sensitizer molecule or by chemical methods.^[1] In contrast to type I photooxygenation (radical type) or type III photooxygenation (electron transfer induced, either involving the reaction between substrate cation radicals and triplet oxygen or the reaction of superoxide radical anion), singlet oxygen reactions are highly selective and show all kinetic properties of pericyclic reactions.^[2] The most important reaction modes are the ene reaction,^[3] the [4 + 2]-^[4] and the [2 + 2]-cycloaddition,^[5] as well as heteroatom oxidation (e.g., sulfide to sulfoxide).^[6] The first three reaction modes represent efficient synthetic routes to a broad variety of oxyfunctionalized products. For practical purposes, singlet oxygen is generated in solution phase by photochemical triplet-triplet sensitization from appropriate dyestuffs. For all relevant solvents, a variety of sensitizers is known and well characterized concerning their chemical stability and singlet oxygen quantum yields.^[7] From the standpoint of green chemistry,^[8] photooxygenation appears to be the most promising oxidation route: the sole oxygen source is natural triplet oxygen and, in contrast to hydrogen peroxide with a maximum atom efficiency of 47%,^[9]

complete atom economy can be reached and both oxygen atoms incorporated in the final products.^[10] The energy source for activating molecular oxygen is simply visible light and, thus, photooxygenation is one of the archetype reactions feasible also for solar chemistry applications.^[11] In order to use photonic energy for converting ground-state into reactive oxygen species, long-wavelength light absorbing dyestuffs can be used which are widely distributed in nature.

Approaches to the Problem

It has been recognized in recent years that in spite of the favorable reactivity pattern of $^1\text{O}_2$, condensed phase photooxygenation conditions suffer from at least five major drawbacks: a) the sensitizer dye must be soluble in the respective solvent, thus limiting the dye-solvent combinations which can be used, b) removal of the dye from the product after the reaction either by chromatography or distillation is often an elaborate process, c) singlet oxygen has its longest lifetimes in environmentally problematic solvents such as halogenated hydrocarbons (tetrachloromethane, freons, etc.),^[12] d) photobleaching of the dye is often observed in halogenated solvents due to the formation of acid or is induced by $^1\text{O}_2$ itself or other oxygenated reactive intermediates, especially when long reaction times are

necessary,^[13] e) solution purging with pure oxygen is highly problematic for industrial applications and sometimes also for small-scale laboratory syntheses. A global solution to all these problems is desirable in order to make photooxygenation a real green chemical process. Another challenge for the singlet oxygen community is to make “chiral singlet oxygen”, i.e., to modify the reaction environment in such a way that matrix effects might imprint stereochemical information in type II reactions.

In order to meet these requirements, several solutions have been considered. Direct activation of triplet oxygen has been described for zeolite irradiation in the presence of adsorbed alkenes,^[14] presumably through low-energy oxygen-alkene CT complexes.^[15] The regioselectivity of singlet oxygen ene-reactions can be modified in the supercages of NaY zeolites,^[16] a phenomena which has been widely explored in the last years.^[17] Photooxygenation of an alkene in the presence of ephedrine as chiral inductor was performed in an NaY zeolite yielding hydroperoxides with low enantioselectivities.^[18] In these cases, the singlet oxygen sensitizers are simply co-adsorbed in the zeolite supercages. Likewise, sensitizer molecules can be incorporated into nafion membranes,^[19] an approach which enables the spatial separation of dye and substrate. The use of microcontainers (micelles, vesicles) for photochemical transformations has also been recently explored for photooxygenations.^[20] In contrast to these approaches, polymer-bound sensitizers have been developed quite early, initially with polystyrene-bound rose bengal.^[21] Recently, numerous variations have been reported, e.g., ionic porphyrins immobilized on cationically functionalized polystyrene as photosensitizers,^[22] pyrylium salts immobilized on Merrifield resins as electron-transfer sensitizers,^[23] polystyrene-bound benzophenones as immobilized triplet photosensitizers,^[24] photosensitizers ionically bound at polymeric ion exchanging resins,^[25] polymer-bound ruthenium(II) complexes,^[26] and polyethylene glycol supported tetra(hydroxyphenyl)-substituted porphyrins.^[27]

The combination of a microreactor system as the reaction medium and visible light as reagent offers a new and convenient approach towards green photochemistry, where not only the production of side products is retarded as a result of the enhanced selectivity but also the use of microcontainers reduces the amounts of environmentally problematic and expensive solvents. The term microcontainer refers to organized and constrained media which provide microcavities and/or surfaces to accommodate the substrates and allows the reaction to take place. In a recent communication, we have described the use of tetraarylporphyrin sensitizers embedded in a commercially available polystyrene-divinylbenzene (PS-DVB) copolymer as reaction medium for photooxygenation reactions.^[28] The experimental protocol for singlet oxygen ene reactions and

[4 + 2]-cycloadditions is described now in detail in this contribution and, additionally, the synthesis and application of insoluble polymer-bound, sensitizer-loaded, nanosized particles as containers for solvent-free type II photooxygenation are described and compared with the results of solution photochemistry. A highly important industrial application of singlet oxygen ene reactions is the photooxygenation of citronellol as a route to the fragrant chemical specialty rose oxide,^[29] and thus this reaction is used as one of the model process.

Results and Discussion

The solubility of the excellent singlet oxygen sensitizers of the *meso*-tetraarylporphyrin-type (e.g., $\phi_{\Delta} = 0.89$ for TPP in benzene)^[30] is low in aprotic polar solvents and even lower in protic solvents. Therefore, the best way for product isolation from the crude reaction mixture is extraction with a protic solvent such as ethanol or methanol. On the other hand, tetraarylporphyrins and hematoporphyrins are known to quench singlet oxygen,^[31] and thus must not be applied in high concentrations in solution where they tend to dimer formation and increased singlet oxygen quenching. Two solutions were developed in our group to circumvent these problems in reaction processing: 1) the microcontainer approach where substrate and sensitizer are dissolved in the polystyrene matrix and irradiated in the presence of air, and 2) the use of polymer-bound tetraarylporphyrin-sensitizers with the substrate likewise dissolved in the matrix and irradiated. These processes are described below in detail.

Polystyrene Matrix with Adsorbed Singlet Oxygen Sensitizer

The singlet oxygen photooxygenation is performed with the organic substrate embedded in commercially available polystyrene-divinylbenzene beads ($60 \pm 15 \mu\text{m}$ diameter unswelled). The non-polar sensitizer (*para*-substituted *meso*-tetraarylporphyrins or the parent *meso*-tetraphenylporphyrin TPP) for the generation of singlet oxygen was transferred in catalytic amounts into the polystyrene network by swelling the resin with a solution of the sensitizer in dichloromethane (or in secondary cycles also with ethyl acetate) and subsequent evaporation of the solvent. As investigated in detail, the polystyrene beads change their space structures while swelling with a non-polar solvent.^[32] After swelling with ethyl acetate, an average bead diameter of $120 \pm 25 \mu\text{m}$ was determined by optical microscopy (Figure 1).^[33] In the polystyrene-matrix, the sensitizer to substrate molar ratio was typically 1:1000, but also ratios as low as 1:5000 were still effective. The substrate was transferred to the polymer beads by the same procedure. Depending

on the polarity and the volatility of the substrate, the polystyrene beads can be loaded with 80–120 wt %. After evaporation of the excess solvent, a layer of sandy solid was obtained which was irradiated in a loosely covered petri dish by means of a sodium street lamp or a halogen lamp without external cooling or purging with oxygen. After irradiation, the product was extracted from the polymer beads by repeated washing with ethanol. Due to the extreme low solubility of *meso*-tetraarylporphyrins in more polar solvents the sensitizer stayed nearly completely in the solid support and the substrate loading process could be repeated. The loading, photolysis and the unloading process were repeated five times with citronellol (**1**) without noticeable sensitizer bleaching or decreasing of the efficiency. Citronellol gave the hydroperoxide mixture **2a:2b** in 95–98% yields without need for purification in the same regio- and stereoisomeric composition as in non-polar solvents (Scheme 1). Under solvent-free conditions the degree of conversion was comparable to the solution photooxygenation in tetrachloromethane. We investigated several additional examples for the ene-reaction and [4 + 2]-cycloaddition and found that in many cases the reactivity and selectivity behavior are identical to those of solution photochemistry: the highly reactive α -pinene **3** gave the allylic hydroperoxide **4** in excellent yields and the singlet oxygen [4 + 2]-cycloaddition with sorbinol (**5**)^[34] proceeded with high yields and negligible substrate loss in the polystyrene matrix. The regiochemistry of the singlet oxygen addition to mesitylol (**9a**) was unaffected by the polymer support, however, the diastereoselectivity of this hydroxy-directed ene reaction^[35] showed to be strongly dependent on the environment: the *syn:anti*-ratio changed from 1.5:1 in ethanol, 3:1 in polystyrene to 10:1 in tetrachloromethane, indicating strong intermolecular hydrogen-bonding between substrate (**9a**) molecules in the unpolar matrix. The chiral diene alcohol **11** gave the endoperoxides *syn*- and *anti*-**11**^[36] in acceptable yields but low diastereoselectivity. Even less reactive substrates like β -pinene (**3**) and ethyl tiglate^[28] were transformed into the corresponding allylic hydroperoxides with complete conversion.

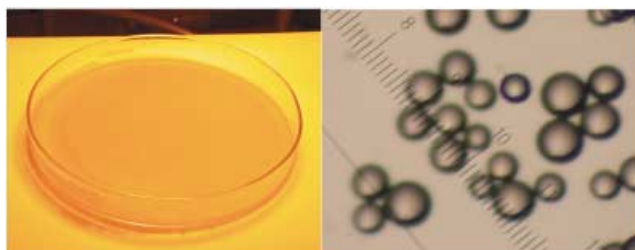
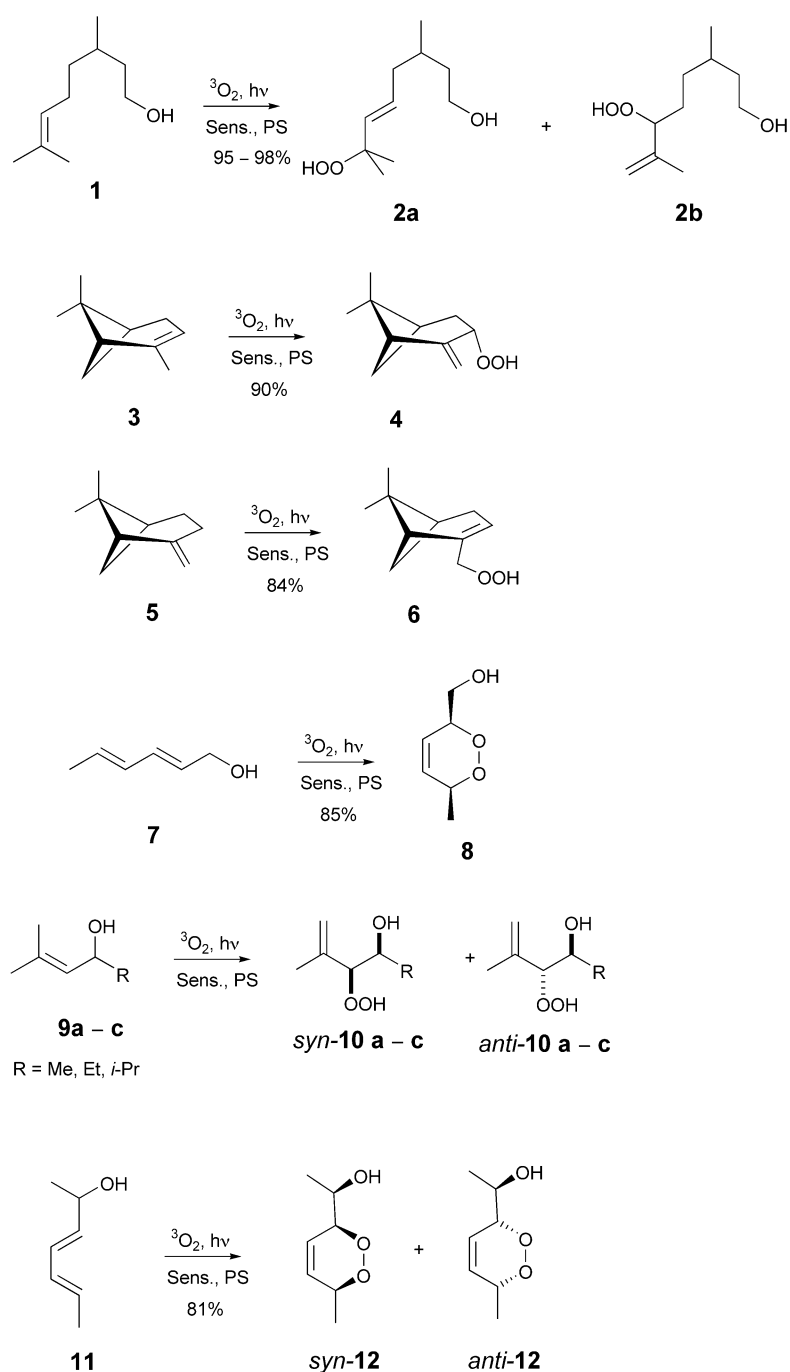


Figure 1. Left: TTP-loaded polystyrene beads (swollen with EtOAc and treated with **1**) in a petri dish, irradiated with a halogen lamp; right: polymer beads with substrate (**1**) and TPP (PS-DVP-TPP), average bead diameter 120 μm .

Polystyrene Matrix with Covalently Linked Singlet Oxygen Sensitizer

For the second approach, tetrakis(4-ethenylphenyl)porphyrin (tetraarylporphyrin, TSP) was synthesized^[37] and copolymerized with styrene and divinylbenzene (DVB). The technique used therefore is emulsifier-free emulsion polymerization, allowing the synthesis of the resin particles readily and with high reproducibility. The TSP-PS-DVB resin beads are translucent nanoparticles (size range 150–300 nm).^[38] The polymer beads show high mechanical stability and behave as inexpensive, highly efficient and resistant sensitizers. They show (like other commercial polystyrene resins) high loading capacity due to the large surface area. They are also easily and efficiently recycled with photooxygenation turnover numbers up to 3000 without any sensitizer bleaching or bleeding. It is especially worthy of mention that the polymer matrix was stable even against the potential oxidants produced during the photooxygenation (hydroperoxides or endoperoxides). The solvent-free photooxygenation procedure using the polymer-bound sensitizer follows the same protocol as with the non-covalently bound sensitizer.

In order to explore the potential of the new TSP-PS-DVB solvent-free photooxygenation procedure and identify its influence on the chemo-, regio- and stereoselectivity pattern in the type II photooxygenation reaction, the same substrates for both ene and [4 + 2]-cycloaddition reactions with singlet oxygen have been investigated as described above for the polystyrene resin with non-covalently bound sensitizer. The diastereoselectivity of both the ene and [4 + 2]-cycloaddition reactions of $^1\text{O}_2$ was investigated using the chiral allylic alcohols **9a–c** and the chiral dienol **11**,^[36] respectively. The photooxygenation of **9a–c** (Table 1) yielded the *syn*-hydroxy allylic hydroperoxide as the major diastereoisomers referring to the hydroxy-directing effect of $^1\text{O}_2$ in the conformationally fixed (by $^{1,3}\text{A}$ -strain) substrates.^[35] Both the polymer-bound as well the free sensitizer systems gave similar diastereoselectivity (with the polymer-bound sensitizer somewhat higher), however considerably lower than in non-polar solvents (photooxygenation of **9a** in CCl_4 proceeds with a diastereoselectivity of 93%). Intermolecular hydrogen-bonding between the highly concentrated substrate molecules in both microcontainer systems accounts for the decrease in diastereoselectivity; this assumption was further supported by the fact that photooxygenation of **9a** in a rose bengal/cellulose acetate film (showing additional intermolecular hydrogen-bonding between the matrix and the substrates) results in even lower diastereoselectivity (dr: *syn:anti* 70:30) in comparison with the photooxygenation carried out either in the sensitizer-bound or free sensitizer PS-DVB matrices.^[39] In order to estimate the percentage of TSP covalently bound in the TSP-PS-



Scheme 1. Photooxygenation of substrates in polystyrene (PS) matrices.

DVB resin, two parallel photooxygenation reactions were run using identical amounts of the synthesized TSP-PS-DVB resin and the commercially available PS-DVB copolymer (loaded with a given amount of the sensitizer). Both reactions were carried out under identical reaction conditions using identical amounts of **9b**. From the comparison of the degrees of conversion in both experiments, a loading degree of 0.1% TSP in the polystyrene resin was determined. For both reaction setups (adsorbed porphyrins as well as covalently

linked dyestuff) an average loading degree of $1 - 2 \mu\text{mol g}^{-1}$ is adjusted.

Conclusion

In summary, two effective, environmentally friendly protocols for type II (singlet oxygen) photooxygenation reactions were developed. The new solvent-free method utilizes only atmospheric oxygen as oxidant and a

Table 1. Singlet oxygen ene reaction with the chiral allylic alcohols **9a–c**.

Entry	R	TSP-PS-DVB dr (<i>syn:anti</i>) ^[a]	Commercial PS-DVB-TPP dr (<i>syn:anti</i>) ^[a]
a	CH ₃	81:19	75:25
b	Et	78:22	77:23
c	<i>i</i> -Pr	82:18	81:19

^[a] dr values were calculated by ¹H NMR from the crude reaction mixture.

synthetic porphyrin-linked resin as reaction medium. Sensitizer characterization and application on different substrates were discussed and compared with solution photooxygenation and other commercial polystyrene resin systems.

Experimental Section

TPP (*meso*-tetraphenylporphyrin) and TTP (*meso*-tetrakis-4-methylphenylporphyrin) were purchased from Porphyrin Systems. Polystyrene beads (1% divinylbenzene copolymer, 100–200 mesh) were purchased by Acros Organics.

General Procedure for Route 1: Photooxygenation of Citronellol (**1**)

A slurry of 3 g of polystyrene beads with a solution of 2 mg (3×10^{-3} mmol) of tetraphenylporphyrin and 780 mg of citronellol (**1**, 5 mmol) in 30 mL of dichloromethane was dispensed on a petri dish (Ø19 cm). The excess solvent was evaporated by leaving the petri dish for a few minutes in a well ventilated hood. The sandy solid which was obtained was irradiated for 5 h in the loosely covered petri dish by a sodium street lamp or a halogen lamp without external cooling and without external oxygen purging. The polymer beads were subsequently rinsed with 3×20 mL of ethanol and filtered. After evaporation of the solvent, the product was obtained as a 1:1.1 mixture of the two regioisomers **2a,b**; yield: 900 mg (96%). The residual polystyrene beads could be used for five additional photooxygenations; advantageously, ethyl acetate was used instead of dichloromethane for all further photooxygenation reactions.

(E)-7-Hydroperoxy-3,7-dimethyloct-5-en-1-ol (2a) and 6-hydroperoxy-3,7-dimethyloct-7-en-1-ol (2b): 1.2:1 mixture of regioisomers, **2b** as a 1:1 mixture of diastereoisomers (estimated from the ¹³C NMR signal intensities):^[40] ¹H NMR (300 MHz, CDCl₃): δ = 0.85 (d, *J* = 6.5 Hz, 3H, CHCH₃), 0.87 (d, *J* = 6.4 Hz, 3H, CHCH₃), 1.2–1.7 (m, 10H, CH₂CHCH₂), 3.64 (m, 4H, CH₂OH); characteristic signals for **2a**: δ = 1.29 [s, 6H, COOH(CH₃)₂], 5.51 (d, *J* = 15.8 Hz, 1H, COOHCH=CH), 5.63 (m, 1H, COOHCH=CH); characteristic signals for **2b**: δ = 1.65 (s, 3H, C_qCH₃), 1.95 (m, 2H, COOHCH₂), 4.24 (m, 1H, CHOOH), 4.95 (s, 2 H, C_q=CH₂); ¹³C NMR (75.5 MHz, CDCl₃): characteristic signals for **2a**: δ = 19.7 (q, 1C, CH₃CH₃), 28.0 (d, 1C, CH₃CH), 29.5 [q, 2C, CH(CH₃)₂], 38.9 (t, 1C, CH=CHCH₂), 39.7 (t, 1C, CH₂CH₂OH), 60.8 (t, 1C, CH₂OH), 81.9 (s, 1C, COOH), 129.8 (d, 1C, COOHCH=CH),

135.0 (d, 1C, COOHCH=CH); characteristic signals for **2b**: δ = 16.9/17.0 (q, 1C, C_qCH₃), 19.4/19.5 (q, 1C, CHCH₃), 24.2/24.3 (t, 1C, COOHCH₂), 28.3/29.2 (d, 1C, CHCH₃), 32.5/32.7 (t, 1C, COOHCH₂CH₂), 39.3/39.5 (t, 1C, CH₂CH₂OH), 60.8 (t, 1C, CH₂OH), 89.4/89.8 (d, 1C, CHOOH), 113.8/114.2 (t, 1C, C_q=CH₂), 143.7/143.9 (s, 1C, C_q).

(3,6-Dihydro-6-methyl-1,2-dioxin-3-yl)methanol (8):^[34]

¹H NMR (300 MHz, CDCl₃): δ = 1.13 (dd, *J* = 6.7 Hz, *J* = 1.32 Hz, 3H, CH₃), 3.78 (m, 1H, CH₂OH), 3.60 (m, 1H, CH₂OH), 4.37 (m, 1H, CH₂OHCH), 4.72 (m, 1H, CHCH₃), 5.79 (m, 1H, CH₂CHCH=CH), 5.89 (m, 1H, CH=CHCHCH₃); ¹³C NMR (75.5 MHz, CDCl₃): δ = 17.5 (q, 1C, CH₃), 63.0 (d, 1C, COH), 74.3 (d, 1C, CH₃CH), 79.7 (d, 1C, CH₂OHCH), 122.9 (d, 1C, CH₂CHCH), 131.2 (d, 1C, CHCHCH₃).

1-(6-Methyl-3,4-dihydro-[1,2]dioxin-3-yl)-ethanol (12):^[36]

Diastereoisomeric ratio = 1.1:1; signal assignments by peak intensities and ¹H-¹³C-COSY. Major diastereomer: ¹H NMR (300 MHz, CDCl₃): δ = 1.21 (d, *J* = 5.1 Hz, 3H, CH₃CHOO), 1.22 (d, *J* = 6.4 Hz, 3H, CHOHCH₃), 4.07 (m, 1H, CHOH), 4.20 (m, 1H, CHOHCH), 4.69 (dq, *J* = 6.8 Hz, 1.8 Hz, 1H, CH=CHCHCH₃), 5.99 (m, 2H, CH=CH); ¹³C NMR (75.5 MHz, CDCl₃): δ = 17.8 (q, CH₃CHOO), 19.0 (q, CH₃CHOH), 68.2 (d, COH), 74.3 (d, CH₃CHOO), 81.6 (d, CHOHCH), 122.7 (d, CH=CHCHCH₃), 130.9 (d, CH=CHCHCH₃). Minor diastereomer: ¹H NMR (300 MHz, CDCl₃): δ = 1.14 (d, *J* = 6.7 Hz, 3H, CH₃CHOO), 1.19 (d, *J* = 4.9 Hz, 3H, CHOHCH₃), 3.96 (m, 2H, CHOHCH), 4.78 (dq, *J* = 6.7 Hz, 1.3 Hz, 1H, CH=CHCHCH₃), 5.86 (m, 1H, CH=CHCHCH₃), 5.90 (m, 1H, CH=CHCHCH₃); ¹³C NMR (75.5 MHz, CDCl₃): δ = 17.3 (q, CH₃CHOO), 18.0 (q, CH₃CHOH), 69.9 (d, CHOH), 74.2 (d, CH₃CHOO), 83.2 (d, CHOHCH), 123.2 (d, CH=CHCHCH₃), 130.9 (d, CH=CHCHCH₃).

5,10,15,20-Tetrakis(4-ethenylphenyl)-21H,23H-porphine (tetrastyrilporphyrin, TSP)

TSP could be synthesized either by Wittig reaction of 5,10,15,20-tetrakis(4-formylphenyl)porphyrin (prepared from terephthalaldehyde and pyrrole)^[37] with methyltriphenylphosphonium bromide or by dehydrohalogenation of 5,10,15,20-tetrakis-[4-(2-haloethyl)-phenyl]porphyrin (prepared from 4-(2-haloethyl)benzaldehyde and pyrrole).^[41] The latter process appeared advantageous because of higher yields and better reproducibility.

Polymerization of Tetrastyrilporphyrin with Styrene and Divinylbenzene

Deionized water (200 mL), acidified to pH = 2.3 with sulfuric acid, was purged with nitrogen and heated to 70 °C for 20 min in a 500-mL three-necked flask equipped with stopper, reflux condenser and gas inlet. Subsequently, 10 g of styrene, 100 mg of divinylbenzene and 10 mg of TSP were added rapidly and the system was sealed in order to prevent contamination with air. While the mixture was being vigorously stirred, 120 mg of potassium peroxodisulfate in 10 mL of water were added at once. After a polymerization period of 7 h, the reaction mixture was quenched with 200 mL of methanol and then cooled to room temperature. The polymer particles were

separated by centrifugation at 3500 rpm, washed with methylene chloride several times to remove any free (non-polymerized) TSP, and dried at 40 °C under vacuum to afford the polymer-bound sensitizer; yield: 4.2 g (42%).

General Procedure for Route 2: Photooxygenation of 5-Methylhex-4-en-3-ol (9b)^[42]

The dye-cross-linked polymer beads (0.60 g) were added into a petri dish (14 cm diameter) and treated with 20 mL methylene chloride, subsequently with 0.50 g of 5-methylhex-4-en-3-ol (4.5 mmol) dissolved in 20 mL ethyl acetate and the excess solvent was evaporated. The petri dish was covered with a glass plate and irradiated with a 150 W halogen lamp for 42 h. The product was extracted with 2 × 30 mL of methanol and filtered. After evaporation of the solvent and purification by column chromatography, the hydroperoxide **10b** was isolated; yield: 0.44 g (69%); dr (*syn:anti*) = 78:22. *Syn*-diastereoisomer: ¹H NMR (300 MHz, CDCl₃): δ = 0.89 (t, 3H, *J* = 7.42 Hz, CH₂CH₃), 1.17–1.52 (m, 2H, CH₂CH₃), 1.65 (s, 3H, CH₃), 3.52 (ddd, 1H, *J* = 8.53, 8.53, 3.24 Hz, CH-OH), 4.12 (d, 1H, *J* = 8.53 Hz, CH-OOH), 4.97 (m, 2H, =CH₂); ¹³C NMR (75.5 MHz, CDCl₃): δ = 9.5 (q, CH₂CH₃), 17.7 (q, CH₃C=), 25.4 (t, CH₂), 71.7 (d, CH-OH), 93.4 (d, CH-OOH), 116.3 (t, =CH₂), 141.5 (s, Cq). *Anti*-diastereoisomer: ¹H NMR (300 MHz, CDCl₃): δ = 0.90 (t, 3H, *J* = 7.42 Hz, CH₂CH₃), 1.17–1.52 (m, 2H, CH₂CH₃), 1.73 (s, 3H, CH₃), 3.65 (m, 1H, CH-OH), 4.27 (d, 1H, *J* = 4.55 Hz, CH-OOH), 5.00 (m, 2H, =CH₂); ¹³C NMR (75.5 MHz, CDCl₃): δ = 10.2 (q, CH₂CH₃), 19.2 (q, CH₃C=), 24.9 (t, CH₂), 72.1 (d, CH-OH), 91.3 (CH-OOH), 115.1 (t, =CH₂), 141.2 (s, Cq).

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